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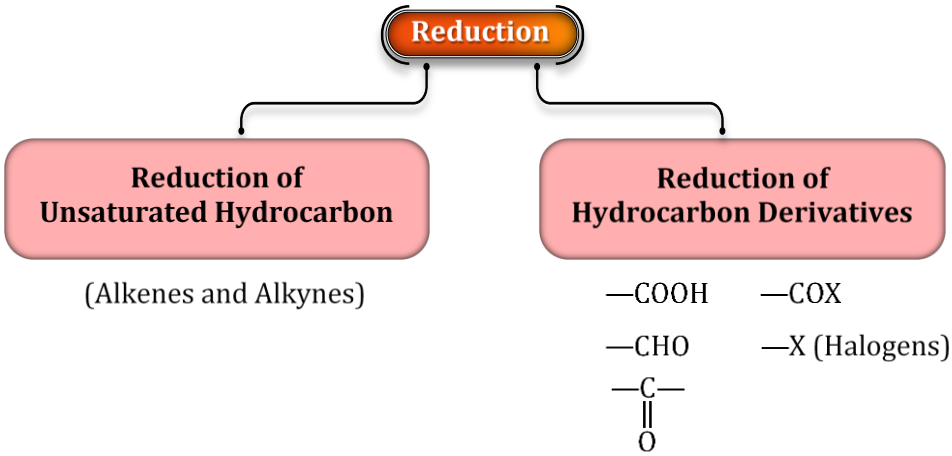
04 Hydrocarbons

Alkane

Methods of Preparation of Alkane

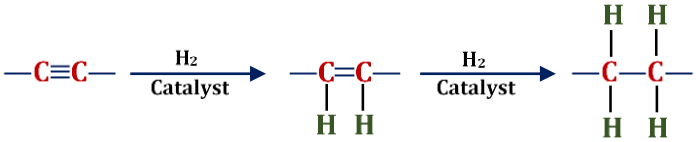
1. Reduction

Addition of hydrogen or removal of N, O, X



(i) From Alkenes and Alkynes (Reduction)

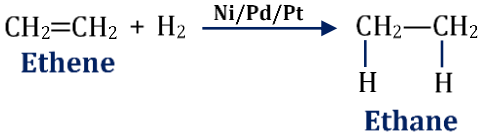
When alkenes and alkynes are completely hydrogenated in the presence of a metal catalyst, alkane is formed and addition of hydrogen is syn (same side)

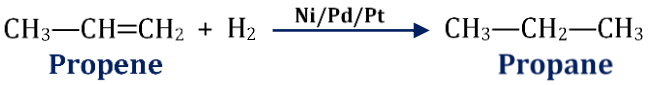


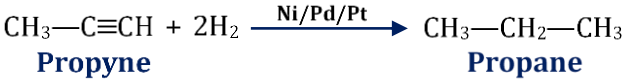
Catalyst :

(a) Pd/Pt at ordinary temperature and pressure.
(b) Ni, 200–300° C (Sabatier and Senderens reaction)
(c) Raney Nickel (Fine grains of Ni–Al) at room temp.

Example :







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(ii) By Reduction of Halide

$$R—X \xrightarrow{\text{Reducing agent}} R—H$$

Reducing agents may be

Zn + HCl
Sn + HCl
Fe + HCl
Zn + CH_3COOH

} Metal + acid

Example :

$$CH_3—CH_2—Cl \xrightarrow{Zn + HCl} CH_3—CH_3$$

$$CH_3—CH_2—CH_2—Cl \xrightarrow{Zn + HCl} CH_3CH_2CH_3$$

(iii) By Reduction of Aldehyde/ Ketone

(A) Clemmensen Reduction

Reagent : Zn-Hg/Conc. HCl

Function : Aldehyde/Ketone to Alkane

$$CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow[\Delta]{\text{Zn–Hg/Conc. HCl}} CH_3—CH_2—CH_3$$

In this reaction $—\overset{\overset{O}{\|}}{C}—$ is converted into $—CH_2—$ (Methylene).

(B) Wolff-Kishner Reduction

Reagent : $NH_2NH_2/\overset{\ominus}{O}H$

$$+ \begin{array}{l} CH_2—OH \\ | \\ CH_2—OH \end{array}$$

Function : Aldehyde/Ketone to Alkane

$$CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow[\Delta]{NH_2NH_2/\overset{\ominus}{O}H} CH_3—CH_2—CH_3 + N_2$$

In this reaction $—\overset{\overset{O}{\|}}{C}—$ is converted into $—CH_2—$ (Methylene).

(iv) By Reduction with Red P + HI / 150°C

HI removes all oxygen and adds hydrogen.

$$—\underset{\underset{O}{\|}}{C}—OH \longrightarrow —\underset{\underset{O}{\|}}{C}—H \longrightarrow —\underset{\underset{OH}{|}}{CH}—H \longrightarrow —\underset{\underset{H}{|}}{CH}—H$$

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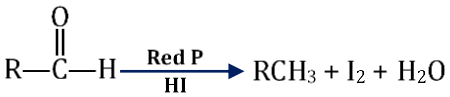
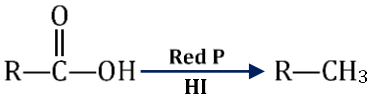
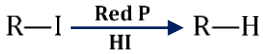






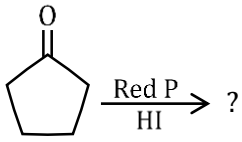
In these reactions, red P is used to remove I_2.

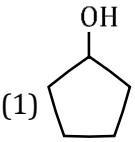
BEGINNER'S BOX-1

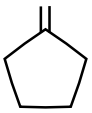
1. The reagent in the Clemmensen's reduction is :-

(1) $LiAlH_4$ (2) Zn-Hg/HCl (3) Zn/HCl (4) Na/EtOH

2.



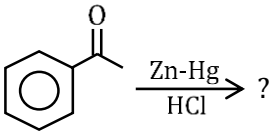
(1) 

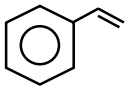
(2) 

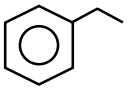
(3)

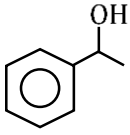
(4)

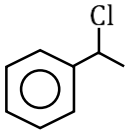
3.



(1) 

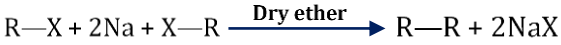
(2) 

(3) 

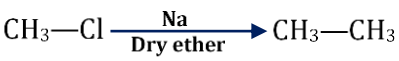
(4) 

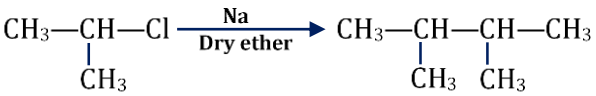
2. Reaction of Haloalkanes with Na

(i) By Wurtz Reaction



Example :

(1) 

(2) 

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Note:

(1) Reactivity order of alkyl halide:- R–I > R–Br > R–Cl > R–F

(2) We can form only symmetrical alkanes having even number of carbon atoms.

H_3C–CH_3 Symmetrical (Even number of carbons)

$H_3C—CH_2$–$CH_2—CH_3$ Symmetrical (Even number of carbons)

H_3C–$CH_2—CH_3$ Unsymmetrical (Odd number of carbons)

H_3C–$CH(CH_3)—CH_3$ Unsymmetrical (Even number of carbons)

Mixed-Wurtz reaction

$$CH_3—Br + CH_3—CH_2—Br \xrightarrow[Et_2O]{Na} CH_3—CH_3 + CH_3—CH_2—CH_2—CH_3 + CH_3—CH_2—CH_3$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3—CH_3$$

$$CH_3—\dot{C}H_2 + \dot{C}H_2—CH_3 \longrightarrow CH_3CH_2—CH_2CH_3$$

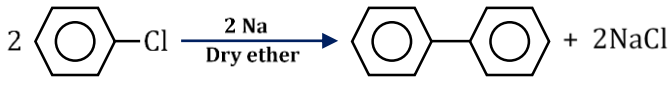
$$\dot{C}H_3 + \dot{C}H_2—CH_3 \longrightarrow CH_3—CH_2CH_3$$

- If two different alkyl halides are used, then it is known as mixed-wurtz reaction.
- Methane cannot be prepared.

Note:

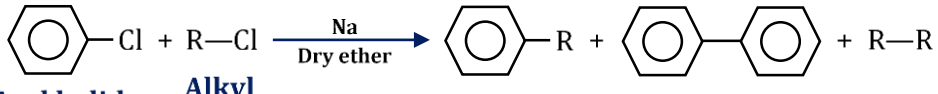
Wurtz reaction is not suitable for preparation of unsymmetrical alkane because in preparation of unsymmetrical alkane mixture of products is obtained which cannot be easily separated.

(ii) Fittig Reaction



Aryl halide Biphenyl

(iii) Wurtz–fittig reaction

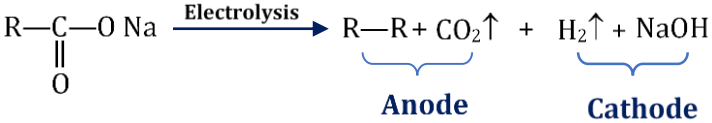


Aryl halide Alkyl halide

3. From Carboxylic Acids

(i) Kolbe's Electrolysis

On electrolysis of sodium/potassium salt of carboxylic acid, generally alkane is obtained as a product.



Anode Cathode

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Note:

- Due to increase in concentration of OH, the pH of solution increases with time during electrolysis.
- CH_4 cannot be prepared.
- H_2 gas is released at cathode and CO_2 gas is released at anode.

(ii) Soda–lime Decarboxylation

Carboxylic acid or sodium salts of carboxylic acids are heated with soda-lime. (NaOH and CaO in 3 : 1 ratio)

Removal of CO_2 from carboxylic acid is known as decarboxylation.

$$CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} CH_4 + Na_2CO_3$$

Or

CH_3COOH

Note:

- In this reaction carbanion intermediate is formed.
- Rate of decarboxylation $\propto$ stability of carbanion.
- Product contains 1C atom less than reactant that's why this reaction is used for stepping down in homologous series.
- CaO is used to keep NaOH dry because it is quite hygroscopic in nature.
- β-keto acid can be easily decarboxylated by heating only (no need of soda-lime)

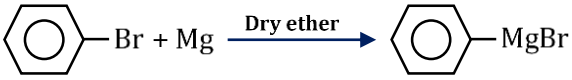
$$\underset{\text{(β-keto acid)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{\Delta} \underset{\text{(Acetone)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-H} + CO_2$$

4. From Grignard Reagent

Preparation of Grignard Reagent

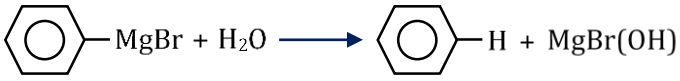
$$R-X + Mg \xrightarrow{\text{Dry ether}} R-MgX$$

$$CH_3-Br + Mg \xrightarrow{\text{Dry ether}} CH_3-MgBr$$



Note:

Grignard reagent behaves like a base and reacts with compounds containing acidic H.



$$CH_3-MgBr + C_2H_5OH \longrightarrow CH_3-H + MgBr(OC_2H_5)$$

Ethanol
(Absolute Alcohol)

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5. From Metal Carbide (By Hydrolysis)

CH_4 can be obtained by the hydrolysis of Be or Al carbides.

$$Al_4C_3 + 12H_2O \xrightarrow{\Delta} 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \xrightarrow{\Delta} 2Be(OH)_2 + CH_4$$

BEGINNER'S BOX-2

1. If two moles of Isopropyl chloride reacts with Na in presence of dry ether. Which alkane is obtained.

(1) Hexane (2) 2, 3-Dimethyl butane

(3) Isopentane (4) Neopentane

2. If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.

(1) n-Butane (2) 2-Methyl butane

(3) 2, 3-Dimethyl butane (4) All of them

3. Which of the following compound can not be obtained from single alkyl halide by wurtz reaction.

(1) Ethane (2) Butane (3) Isobutane (4) Hexane

4. Give reactivity order for decarboxylation ?

(I) $CH_3—CH_2—COOH$ (II) $CH_2=CH—COOH$ (III) $CH\equiv C—COOH$

(1) I > II > III (2) III > II > I (3) III > I > II (4) None is correct

5. Which of the following reaction can not be used to obtained propane in good yield.

(1) Wurtz reaction (2) Corey-house reaction

(3) Decarboxylation of acid salt (4) All of them

6. Decarboxylation of isobutyric acid yields :-

(1) Isobutane (2) Propane

(3) 2-Methyl propane (4) None of the above

7. When alkyl halide is made to react with magnesium in presence of dry ether, alkyl magnesium halide RMgX is formed. To generate R—H the use is made of the reagent :-

(1) RNH_2 (2) ROH (3) NH_3 (4) Any one of the above

Physical Properties of Alkane

1. Solubility

Alkanes being non-polar are insoluble in water but soluble in non-polar solvents like C_6H_6, CCl_4 etc.

2. Boiling Point

Boiling point $\propto$ Molecular weight

$\propto \frac{1}{\text{Branching}}$ (If molecular weight is same)

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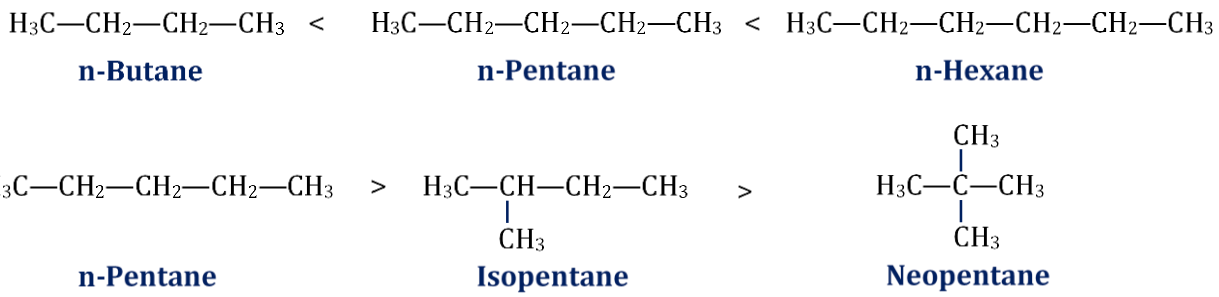
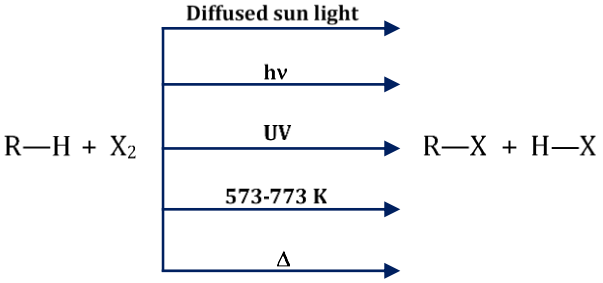


Chemical Properties of Alkane

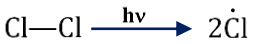
The characteristic reaction of alkanes is Free Radical Substitution Reaction (FRSR)

1. Substitution reaction (Halogenation)



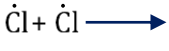
Mechanism

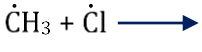
Step-I Chain initiation step



Step-II Chain propagation step

Step-III Chain termination step





Note:

1. Reactivity order of halogen : $F_2 > Cl_2 > Br_2 > I_2$
2. In this reaction, intermediate is carbon free radical.
3. RDS of this reaction is the 1st step of chain propagating step (Abstraction of H).

   Rate of halogenation $\propto$ stability of free radical
4. The order of reactivity of hydrogens towards free radical halogenation is

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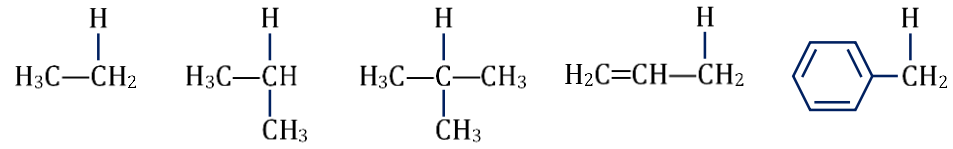
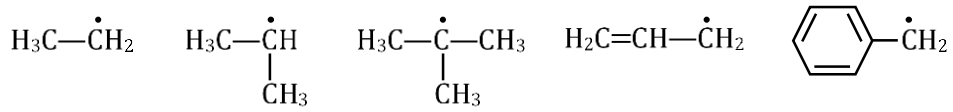


Increasing rate of reaction towards $X_2/h\nu$



5. To avoid Polyhalogenation, alkanes should be taken in excess.

$$\underset{\text{(excess)}}{CH_4} + Cl_2 \xrightarrow{h\nu} CH_3Cl$$

$$CH_4 + \underset{\text{(excess)}}{Cl_2} \xrightarrow{h\nu} CCl_4$$

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$\xrightarrow[h\nu]{Cl_2} CH_2Cl_2 + HCl$$
$$\xrightarrow[h\nu]{Cl_2} CHCl_3 + HCl$$
$$\xrightarrow[h\nu]{Cl_2} CCl_4 + HCl$$

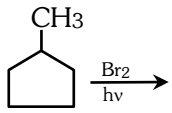
6. Fluorination is explosive in nature, should be carried out in the presence of inert gas like N_2 (inhibitor).
7. Fluorination can take place in dark also.
8. Bromine is less reactive than chlorine so generally requires high temperature.
9. Iodination is reversible so carried out forward in the presence of oxidizing agents like HIO_3, HNO_3, etc.

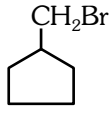
$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

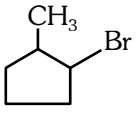
$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$

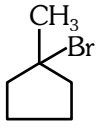
BEGINNER'S BOX-3

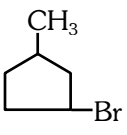
1. In the following reaction, the major product is :-



(1) 

(2) 

(3) 

(4) 

2. The bond dissociation energy at the C–H bond for the compound :-

(I) CH_3H (II) $CH_3 - CH_2 - H$

(III) $CH_2 = CH - CH_2 - H$ (IV) $C_6H_5 - H$

(1) I > II > III > IV (2) IV > III > II > I (3) IV > I > II > III (4) II > I > IV > III

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3. Arrange the following in correct order of reactivity towards $Cl_2/h\nu$ –

(A) CH_4 (B) CH_3CH_3 (C) $CH_3CH_2CH_3$ (D) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}H-CH_3$

(1) A > B > C > D (2) D > C > B > A (3) B > C > A > D (4) C > B > D > A

4. Which of the following are free radical reactions:-

(a) $CH_3CH = CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2-Br$

(b) $CH_3CH = CH_2 + HCl \xrightarrow{\text{peroxide}} CH_3CH(Cl)CH_3$

(c) $CH_3CH = CH_2 + Cl_2 \xrightarrow{500^\circ C} Cl-CH_2CH=CH_2$

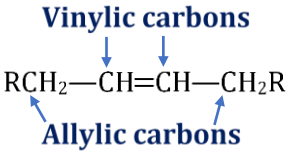
(d) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2Cl$

(1) Only d (2) a, c (3) a, b, d (4) a, c, d

Allylic and Benzylic Substitution Reactions (FRSR)

Allylic and Benzylic Hydrogens

The sp^2 carbons of an alkene are called vinylic carbons. An sp^3 carbon that is adjacent to vinylic carbon is called an allylic carbon. A hydrogen bonded to a vinylic carbon is called a vinylic hydrogen, and a hydrogen bonded to an allylic carbon is called an allylic hydrogen.



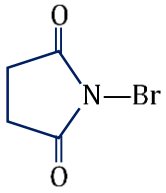
Reagents used for halogenation at allylic and benzylic position.

1. NBS (N-Bromosuccinimide)
2. NCS (N-Chlorosuccinimide)

$$CH_3-CH=CH_2 + NBS \xrightarrow{h\nu} \underset{\displaystyle Br}{\overset{|}{CH_2}}-CH=CH_2$$

$$Ph-CH_3 + NBS \xrightarrow{h\nu} Ph-CH_2-Br$$

It is an example of free radical substitution reaction.



N-Bromosuccinimide

BEGINNER'S BOX-4

1. The compound with the highest boiling point is–

(1) n-hexane (2) n-pentane

(3) 2,2-dimethyl propane (4) Propane

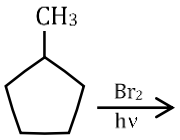
2. Photochemical chlorination of alkane is initiated by a process of

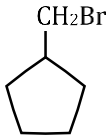
(1) Pyrolysis (2) Substitution (3) Homolysis (4) Peroxidation

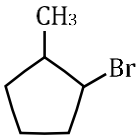
TG: @Chalnaayaaar

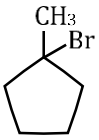
3. Bromination of an alkane as compared to chlorination proceeds
(1) At a slower rate
(2) At a faster rate
(3) With equal rates
(4) With equal or different rate depends upon the temperature

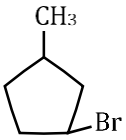
4. In the following reaction, the major product is:



(1) 

(2) 

(3) 

(4) 

5. Arrange the following in correct order of reactivity towards halogenation

(A) CH_4 (B) CH_3CH_3 (C) $CH_3CH_2CH_3$ (D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}-CH_3$

(1) A > B > C > D (2) D > C > B > A (3) B > C > A > D (4) C > B > D > A

2. Combustion reaction

- Alkanes on heating in the presence of excess air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$

$$C_4H_{10}(g) + 13/2O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(\ell)$$

- During incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed.

$$CH_4(g) + O_2(g) \xrightarrow[\text{combustion}]{\text{Incomplete}} C(s) + 2H_2O(\ell)$$

3. Controlled Oxidation

$$2CH_4 + O_2 \xrightarrow[100\ atm]{Cu/523\ K} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$$

(Methanal)

$$2CH_3-CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3-COOH + 2H_2O$$

(Ethanoic acid)

4. Oxidation by $KMnO_4$ or $K_2Cr_2O_7$ (Strong oxidising agent)

Alkanes having 3°H are oxidised in Alcohol

$$CH_3-\overset{3^\circ}{\underset{|}{CH}}-CH_3 \xrightarrow{KMnO_4} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

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5. Isomerisation

Unbranched chain alkanes on heating with $AlCl_3$ + HCl are converted into branched chain alkanes.

$$\underset{\text{n-Butane}}{CH_3—CH_2—CH_2—CH_3} \xrightarrow[\Delta]{AlCl_3 + HCl} \underset{\text{Isobutane}}{CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3}$$

6. Aromatization

n-Alkanes having six or more carbon atoms on heating to 500°C at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina(Al_2O_3) results in the formation of aromatic hydrocarbons.

$$\underset{\text{n-Hexane}}{CH_3(CH_2)_4\,CH_3} \xrightarrow[500°\,C]{Cr_2O_3/Al_2O_3} \underset{\text{Benzene}}{\text{C}_6\text{H}_6} + 4H_2$$

$$\underset{\text{n-Heptane}}{CH_3(CH_2)_5\,CH_3} \xrightarrow[500°\,C]{Cr_2O_3/Al_2O_3} \underset{\text{Toluene}}{\text{C}_6\text{H}_5\text{CH}_3} + 4H_2$$

7. Pyrolysis

- When alkanes are heated to 500-700°C then they are decomposed into lower hydrocarbon. (liquid hydrocarbon is converted in gaseous hydrocarbon)
- This decomposition is known as pyrolysis/cracking.
- It involves free radical elimination.

$$\text{Alkane} \xrightarrow{\Delta} \text{Alkene} + \text{lower alkanes} + H_2$$

$$CH_3CH_2CH_3 \xrightarrow{\Delta} CH_3—CH{=}CH_2 + CH_2{=}CH_2 + CH_3—CH_3 + CH_4 + H_2$$

8. Reaction with steam

Methane reacts with steam at 1273K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of hydrogen gas.

$$CH_4 + H_2O \xrightarrow[1273\ K]{Ni} CO + 3H_2$$

BEGINNER'S BOX-5

1. How many minimum number of carbon should be present in an alkane for aromatization :
(1) 4 (2) 5 (3) 6 (4) 3

2. Which gives 3° Alcohol on oxidation with $KMnO_4/H^+$
(1) $CH_3—CH_2—CH_3$ (2) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ (3) $CH_3—CH_3$ (4) $CH_3—CH_2—CH_2—CH_3$

3. Which is free radical elimination of alkane ?
(1) Isomerization (2) Pyrolysis (3) Halogenation (4) All

TG: @Chalnaayaaar

Alkene

Methods of Preparation of Alkene

1. From Alkynes (By Partial Hydrogenation)

$$R—C\equiv C—R + 2H_2 \xrightarrow{Pd} R—CH_2—CH_2—R$$

(complete hydrogenation)

- Alkynes on reduction in the presence of palladised charcoal partially deactivated with poisons like quinoline etc. give alkenes. (partial hydrogenation)
- Partially deactivated palladised charcoal is known as Lindlar's catalyst.

$$R—C\equiv C—R + H_2 \xrightarrow[\text{Quinoline}]{Pd/C} \underset{H}{\overset{R}{}}\!\!>C=C<\!\!\underset{H}{\overset{R}{}}$$

cis-Alkene

$$R—C\equiv C—R + H_2 \xrightarrow[\text{Lindlar's catalyst}]{Pd/CaCO_3} \underset{H}{\overset{R}{}}\!\!>C=C<\!\!\underset{H}{\overset{R}{}}$$

cis-Alkene

$$R—C\equiv C—R + H_2 \xrightarrow[\text{Rosenmund Catalyst}]{Pd/BaSO_4} \underset{H}{\overset{R}{}}\!\!>C=C<\!\!\underset{H}{\overset{R}{}}$$

cis-Alkene

For partial hydrogenation Birch catalyst (Na + Liq. NH_3) is also used.

Birch reduction

$$\underset{\text{Alkyne}}{R—C\equiv C—R} \xrightarrow[\text{Liq. } NH_3]{\text{Na or Li}} \underset{H}{\overset{R}{}}\!\!>C=C<\!\!\underset{R}{\overset{H}{}}$$

trans-Alkene

Note:

Terminal alkynes do not give Birch reduction.

$$R—C\equiv C—H \xrightarrow[\text{Liq. } NH_3]{Na} R—C\equiv \overset{\ominus}{C}\ \overset{\oplus}{Na} + \frac{1}{2}H_2$$

2. From Alcohols (By Dehydration)

Alcohols on heating with conc. H_2SO_4 give alkenes with the elimination of water molecule. This is known as acid catalysed dehydration of alcohols.

Reagents used: (1) Conc. H_2SO_4/Δ (2) Conc. H_3PO_4/Δ

(3) $KHSO_4/\Delta$ (4) $H^{\oplus}/\Delta$

$$H_3C—\underset{CH_3}{\overset{CH_3}{C}}—OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} H_3C—\underset{CH_3}{\overset{CH_2}{C}} + H_2O$$

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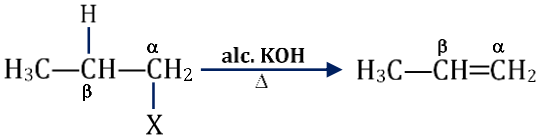
3. From Alkyl Halide (By Dehydrohalogenation)

- Dehydrohalogenation of alkyl halide to form alkene is an example of α, β Elimination reaction because H removes from β-carbon.
- Alkyl halides (R—X) on heating with alcoholic potash eliminate one molecule of halogen acid to form alkenes.

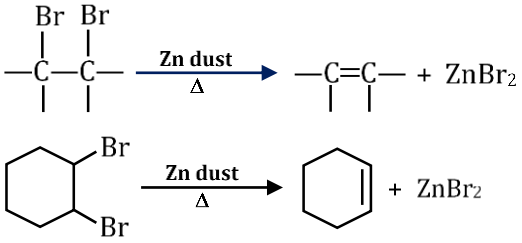


4. Dehalogenation of Vicinal Dihalide

Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides.

Vicinal dihalides on treatment with zinc metal eliminate a molecule of ZnX_2 to form an alkene. This reaction is known as dehalogenation.

Reagent used: Zn dust/Δ

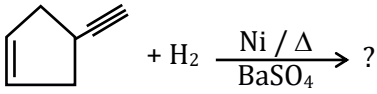


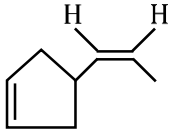
BEGINNER'S BOX-6

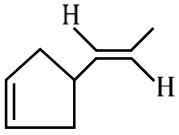
1. Kolbe electrolytic synthesis can be used to obtain all hydrocarbons as a major product except :-
(1) 2-Butene (2) Ethyne (3) Methane (4) Ethene

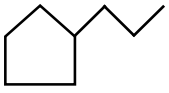
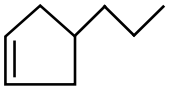
2. Dehydration of alkanol to alkene involves all the steps, except :-
(1) Combination with proton
(2) Formation of carbonium ion by removal of water molecule
(3) Loss of proton from carbonium ion from the β-position
(4) Loss of proton from carbonium ion from α-position

3. When a haloalkane with β-hydrogen is heated with alcoholic solution of KOH the product and the type of mechanism is-
(1) Alcohol, S_N1 (2) Alkene, α-elimination
(3) Alcohol, S_N2 (4) Alkene, β-elimination

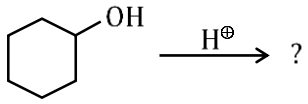
4. 

(1) 

(2) 

(3) 
(4) 

TG: @Chalnaayaaar

5. 

(1) (2) (3) (4)

6. $CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\Delta]{Zn} ?$

(1) $CH_3-C\equiv C-CH_3$ (2) $CH_3-CH=CH-CH_3$

(3) $CH_3-CH_2-C\equiv CH$ (4) $CH_3-CH_2-CH=CH_2$

7. $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\Delta]{\text{Alc. KOH}} ?$

(1) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$ (2) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$

(3) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$ (4) $CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3$

8. Acidic dehydration of alcohol involves :-

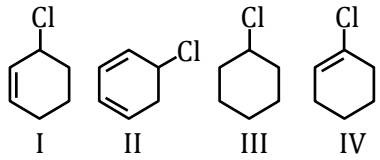
(1) E_1 elimination

(2) Carbocation rearrangement if possible

(3) Saytzeff's product is formed as major product

(4) All

9. Arrange the following in order of their reactivity toward dehydrohalogenation :-



(1) II > I > III > IV (2) III > II > I > IV (3) IV > III > I > II (4) I > II > III > IV

Physical Properties of Alkenes

Physical State

The first three members of alkene are gases, next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell and all other alkenes are colourless and odourless.

Solubility

Alkenes are insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether.

Boiling Point

Alkenes show a regular increase in boiling point with increase in size.

Chemical Properties of Alkenes

Electrophilic Addition Reactions (EAR)

Characteristic reaction of alkene is EAR

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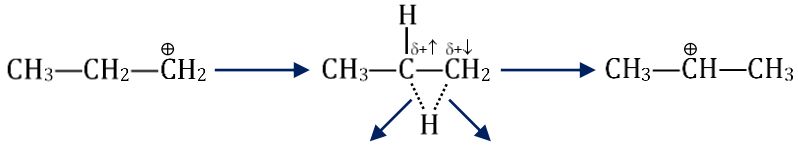
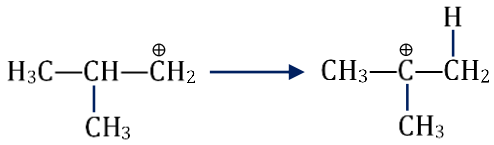
Carbocation Rearrangement

Observed in those reactions in which carbocation is formed as an intermediate.

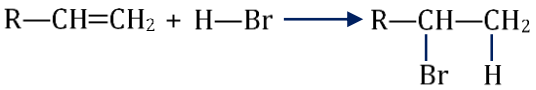
Less stable carbocation rearranges itself to more stable carbocation via transition state.

(1) 

(Transition state : 1, 2 shift)

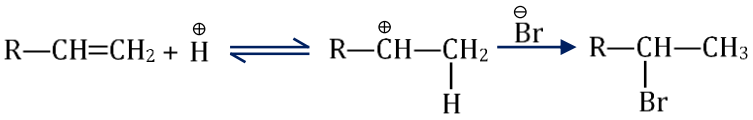
(2) 

1. Reaction with Conc. H—X (Halogen Acid)



(Hydrohalogenation)

Mechanism

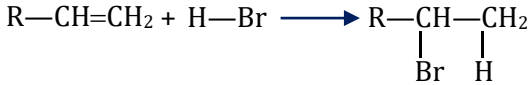


Note:

1. Carbocation intermediate is formed, so make more stable carbocation.
2. Rate of reaction- HI > HBr > HCl > HF

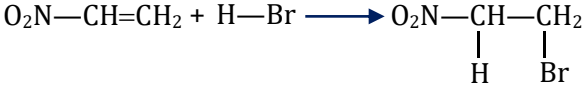
Markovnikov's Rule

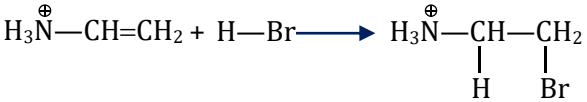
The rule states that negative part of the reagent gets attached to that carbon of double bond which possesses lesser number of hydrogen atoms.



Note:

1. Markovnikov's rule is not applicable if alkene is symmetrical.
   $H_3C—CH=CH—CH_3$
2. Markovnikov's rule is not applicable in the cases where double bonded carbon is directly attached to strong electron withdrawing group like ($–NO_2$, –CHO, $–CCl_3$, $–\overset{\oplus}{N}H_3$)





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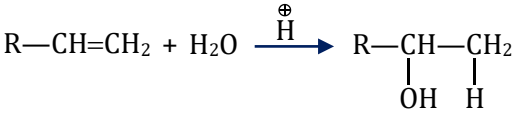
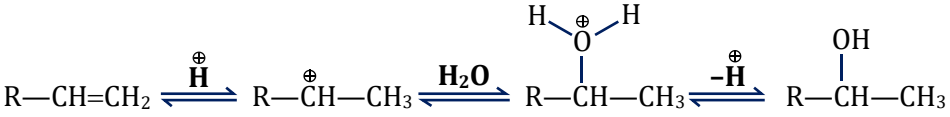
2. Reaction with Dilute H_2SO_4 Or H^+/H_2O Or H_3O^+



(Acidic hydration)

Mechanism

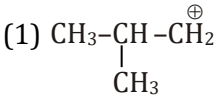


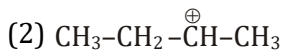
Note:

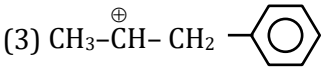
1. Reaction is reversible.
2. Forward reaction is acidic hydration of alkene and backward reaction is acidic dehydration of alcohol (Elimination reaction).

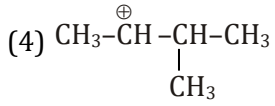
BEGINNER'S BOX-7

1. Which of the following does not show rearrangment :-

(1) 

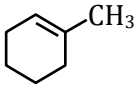
(2) 

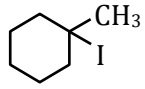
(3) 

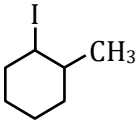
(4) 

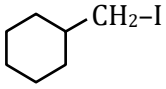
2. The intermediate in the Electrophilic addition–reaction is :-

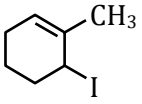
(1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

3.  +HI ⟶ major product is

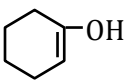
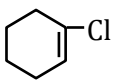
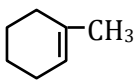
(1) 

(2) 

(3) 

(4) 

4. Give reactivity order towards EAR.

(i) (ii)  (iii)  (iv) 

(1) (i) > (ii) > (iii) > (iv)
(2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (iv) > (i) > (iii)
(4) (iii) > (ii) > (iv) > (i)

5. Which of the following alkene is most reactive for hydration

(1) Ethene (2) Propene (3) 1–butene (4) 2–methyl propene

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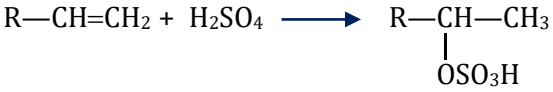
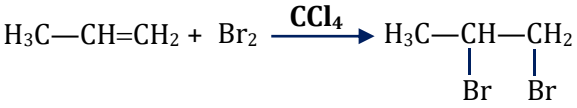
3. Reaction with Conc. H_2SO_4



Alkyl hydrogen sulphate

Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.

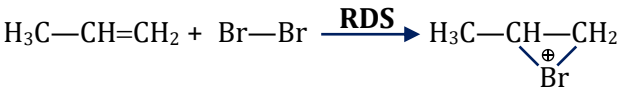
4. Reaction with X_2/CCl_4



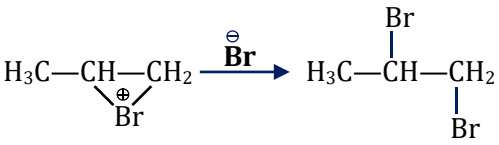
(Halogenation)

Mechanism

(Electrophile has lone pair)

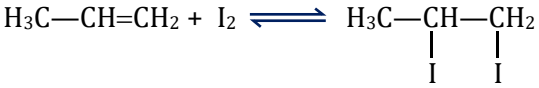


Cyclic Bromonium ion



Note:

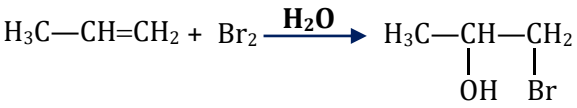
1. Electrophile contains lone pair.
2. No carbocation intermediate is formed so no rearrangement is possible.
3. Reaction intermediate : Cyclic halonium ion.
4. Reactivity of halogens: $F_2 > Cl_2 > Br_2 > I_2$
5. Reaction with F_2 is explosive.
6. Reaction with I_2 is reversible.



7. Test of Unsaturation

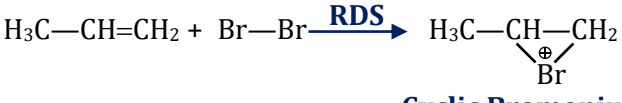
Unknown organic compound $\xrightarrow[CCl_4]{Br_2}$ Reddish brown colour disappears $\rightarrow$ Unsaturation may be present

5. Reaction with X_2/H_2O or HOX (Hypohalous Acid)



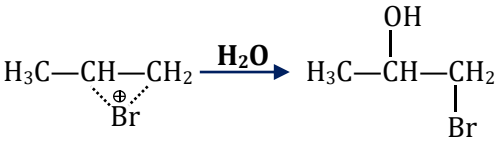
(Halohydrin)

Mechanism



Cyclic Bromonium ion

TG: @Chalnaayaaar



(Major)

Note:

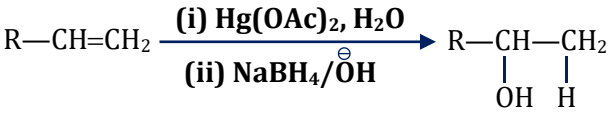
1. No carbocation intermediate is formed so no rearrangement is possible.
2. Reaction intermediate – cyclic halonium ion.

6. Oxymercuration Demercuration (OMDM)

Reagent :

(i) $(CH_3COO)_2$ Hg, H_2O or $Hg(OAc)_2$, H_2O

(ii) $NaBH_4/\overset{\ominus}{O}H$

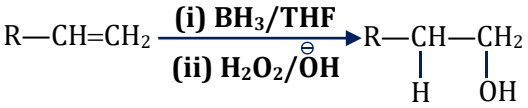


(Alcohol)

Note:

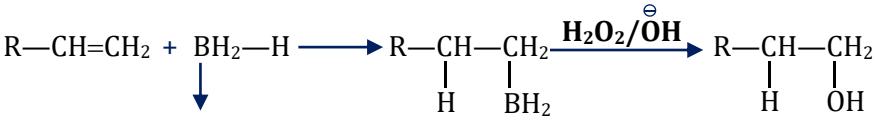
1. In this reaction addition of water takes place and alcohol is formed as a product.
2. No carbocation intermediate is formed so no rearrangement takes place.
3. Markovnikov addition of water takes place.

7. Hydroboration Oxidation (HBO)



(Alcohol)

Mechanism



Electrophile

Anti markovnikov addition

Note:

1. In this reaction addition of water takes place by Anti markovnikov addition of water and alcohol is formed.

2. No carbocation intermediate is formed so no rearrangement takes place.

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BEGINNER'S BOX-8

1. What is the product formed when acetylene reacts with excess hypochlorous acid ?

(1) CH_3COCl (2) $ClCH_2CHO$ (3) Cl_2CHCHO (4) $ClCH_2COOH$

2. Primary alcohol can be formed as major product by

(1) $CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[(2)\ H_2O_2/\overset{\ominus}{O}H]{(1)\ BH_3,THF}$

(2) $CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{dil.\ H_2SO_4}$

(3) $CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[(2)\ NaBH_4]{(1)\ (CH_3COO)_2\ Hg,\ H_2O}$

(4) 2 & 3 both

3. $CH_2=CH_2 + Br_2 \longrightarrow \underset{Br}{\overset{|}{CH_2}}-\underset{Br}{\overset{|}{CH_2}}$ is an example of :-

(1) Electrophilic addition reaction (2) Nucleophilic addition reaction

(3) Free radical addition reaction (4) Free radical substitution reaction

Free Radical Addition Reaction (FRAR)

Peroxide effect / Kharasch effect

$H_3C-CH=CH_2$ —**H—Br**→ $H_3C-\underset{Br}{\overset{|}{CH}}-\underset{H}{\overset{|}{CH_2}}$ **Markovnikov product**

$H_3C-CH=CH_2$ —**H—Br, Peroxide**→ $H_3C-\underset{H}{\overset{|}{CH}}-\underset{Br}{\overset{|}{CH_2}}$ **Anti-Markovnikov product**

"Reaction of alkene with HBr in the presence of peroxide takes place through free radical mechanism and this is an example of Free Radical Addition Reaction (FRAR)"

Peroxide – H_2O_2, ROOR, $C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5$ **(Benzoyl peroxide) etc.**

Mechanism

(i) $R-O\overset{\Delta}{-}O-R \longrightarrow 2R-\dot{O}$

(Peroxide)

(ii) $R-\dot{O} + H-Br \longrightarrow R-OH + \dot{B}r$

(iii) $CH_3-CH=CH_2 + \dot{B}r \longrightarrow CH_3-\underset{Br}{\overset{|}{\dot{C}H}}-CH_2 + CH_3-\underset{Br}{\overset{|}{CH}}-\dot{C}H_2$

2° **1°**

(More stable)

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(iv) $CH_3—\dot{C}H—CH_2 + H—Br \longrightarrow CH_3—\underset{H}{CH}—\underset{Br}{CH_2}+\dot{B}r$

(Major)

Note:

It may be noted that the peroxide effect is not observed in addition of HCl and HI. This is due to the fact that the H—Cl bond being stronger than H—Br bond is not cleaved by the free radical, whereas the H—I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

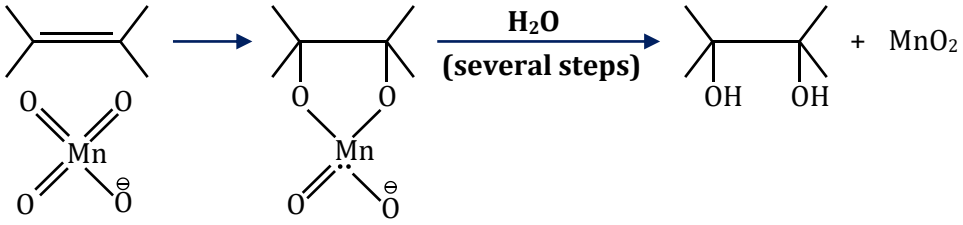
Oxidation

Reactions involving oxidation of carbon-carbon double bond may be classified into two general groups :

1. Oxidation of π bond without cleavage of sigma bond.
2. Oxidation of π bond with cleavage of sigma bond.

1. Oxidation of π bond without cleavage of sigma bond.

Hydroxylation using Baeyer's reagent (cold dilute alkaline $KMnO_4$)

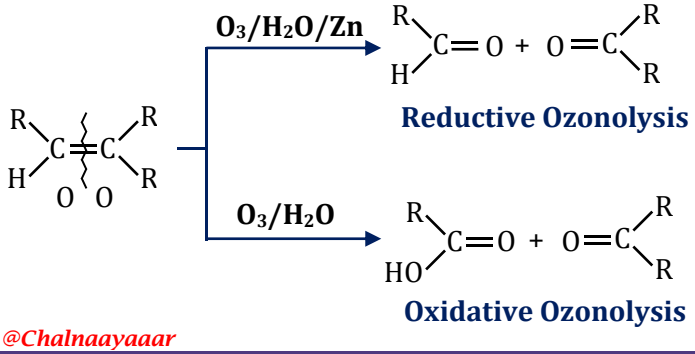


Note:

1. This reaction is also used as test of unsaturation.
2. Baeyer's reagent is purple in colour. As the reaction proceeds, the purple colour disappears and brown precipitate of MnO_2 is observed.

2. Oxidation of π bond with cleavage of sigma bond.

(a) Ozonolysis



Reductive Ozonolysis

Oxidative Ozonolysis

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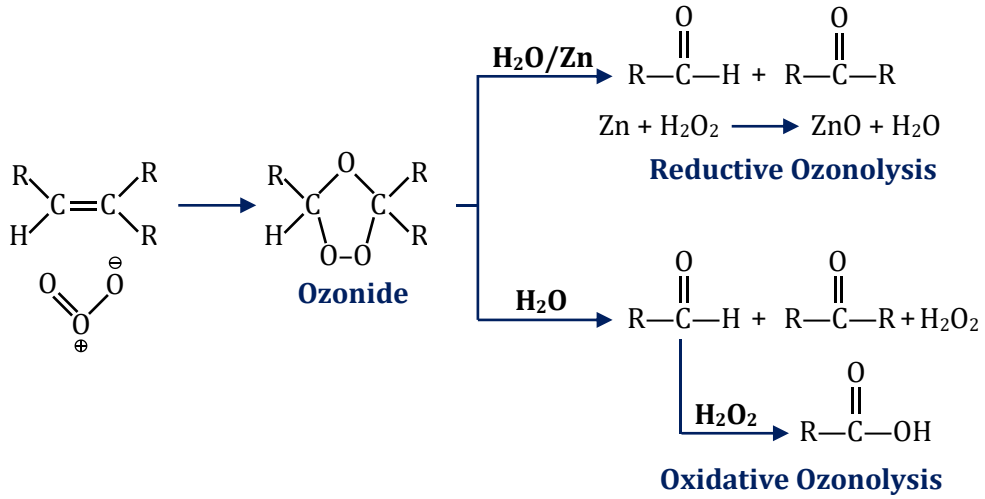
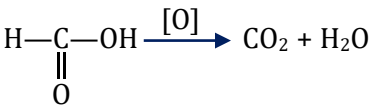


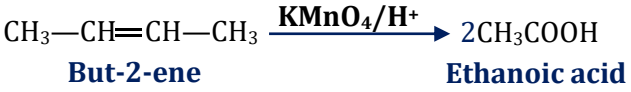
In oxidative ozonolysis further oxidation of aldehyde takes place while oxidation of ketones does not take place.

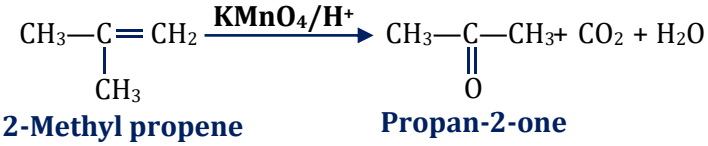
If formic acid is formed in oxidative ozonolysis then it further oxidises into CO_2.



(b) Strong oxidising agent ($KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$)

Acidic $KMnO_4$ or acidic potassium dichromate oxidises alkenes to ketones and acids depending upon the nature of the alkene and the experimental conditions.





BEGINNER'S BOX-9

1. The treatment of $(CH_3)_2C{=}CHCH_3$ with boiling $KMnO_4$ produces

(1) $CH_3COCH_3 + CH_3COOH$ (2) $CH_3COCH_3 + CH_3CHO$

(3) $CH_3CHO + CO_2$ (4) CH_3COCH_3 only

2. An alkene on treating with hot acidified $KMnO_4$ gives 4 - oxopentanoic acid. The alkene is

(1) Pentene (2) 2–Pentene

(3) 1–Methyl cyclobutene (4) 1, 2– Dimethyl cyclopropene

3. The addition of HCl to 3, 3, 3–trichloropropene gives

(1) $Cl_3CCH_2CH_2Cl$ (2) $Cl_3CCH(Cl)CH_3$

(3) $Cl_2CHCH(Cl)CH_2Cl$ (4) $Cl_2CHCH_2CHCl_2$

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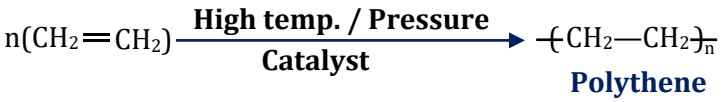
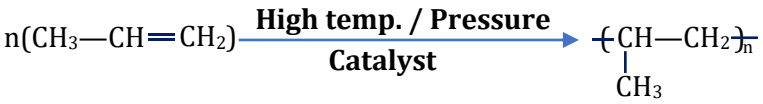
Polymerisation

Polythene is obtained by the polymerisation of ethene molecules at high temperature, high pressure in the presence of a catalyst.

The large molecules thus obtained are called polymers and simple compounds from which polymers are formed are called monomers.



Polythene



Polypropene

Use of Polymers

Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T .V. cabinets etc.

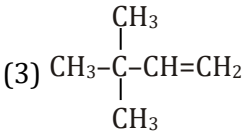
Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles.

BEGINNER'S BOX-10

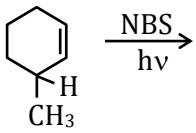
1. Which of the following does not have allylic hydrogen :-

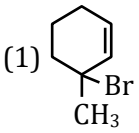
(1) $CH_3—CH=CH_2$

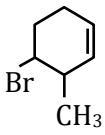
(2) $CH_3—CH_2—CH=CH_2$

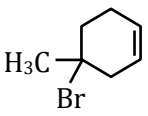
(3) 

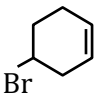
(4) $CH_3—CH=CH—CH_3$

2.  major product will be :-

(1) 

(2) 

(3) 

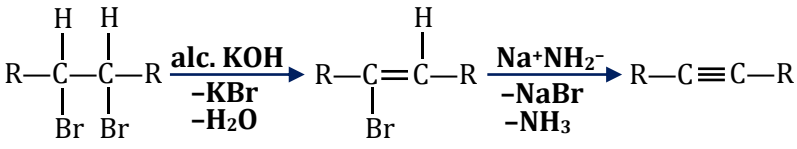
(4) 

Alkyne

Preparation Methods of Alkynes

1. From Vicinal Dihalides

Vicinal dihalides on treatment with alcoholic KOH undergo dehydrohalogenation to form alkenyl halide which on further treatment with sodamide give alkyne.



Vicinal dihalide

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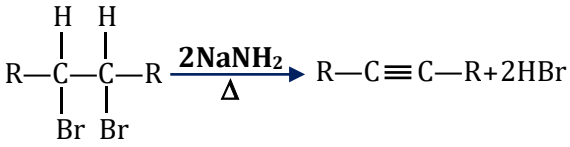
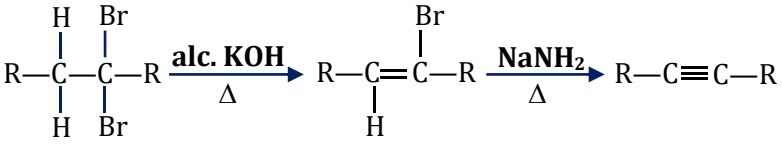
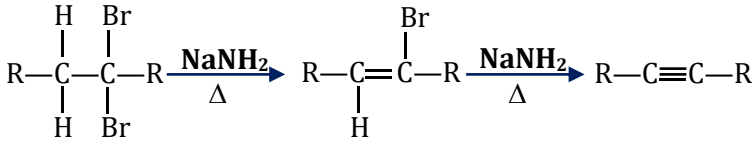


Vicinal dihalide

2. From Geminal Dihalides



Geminal dihalide



Geminal dihalide

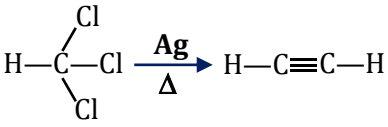
3. From Calcium Carbide

On industrial scale, ethyne is prepared by treating calcium carbide with water.

$CaC_2 + 2H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$

$CaC_2 + 2D_2O \longrightarrow DC{\equiv}CD + Ca(OD)_2$

4. From $CHCl_3/CHI_3$ (Preparation of acetylene)



BEGINNER'S BOX-11

1. $CH{\equiv}CH \xrightarrow{CH_3MgBr} A\ (gas) + B,\ B \xrightarrow{CH_3-I} C$. C is :

(1) CH_4 (2) $CH_3{-}CH_3$ (3) $CH{\equiv}C{-}CH_3$ (4) $CH_3{-}C{\equiv}C{-}I$

2. $CaC_2 + 2D_2O \longrightarrow$ major product will be :-

(1) $CD{\equiv}CD$ (2) $CD_2{=}CD_2$ (3) $CD_3{—}CD_3$ (4) $CH{\equiv}CH$

Physical Properties of Alkynes

(A) First three members are gases, the next eight are liquids and the higher ones are solids.

(B) Ethyne has characteristic odour, other members are odourless.

(C) Alkynes are weakly polar in nature so insoluble with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.

(D) Their melting point, boiling point and density increase with increase in molar mass.

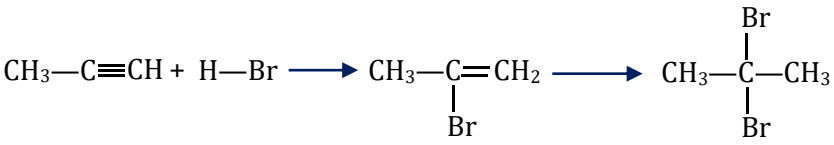
TG: @Chalnaayaaar

Chemical Properties of Alkynes

Addition Reaction R—C≡C—R

1. Addition of hydrogen halides

Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form gem dihalides (in which two halogens are attached to the same carbon atom).

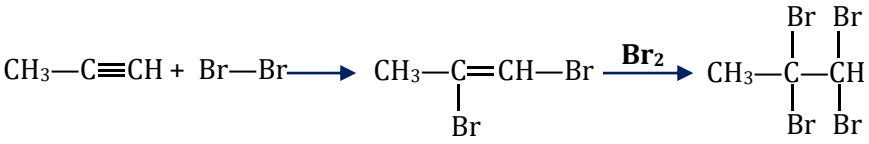


2-Bromopropene **2,2-Dibromopropane**

Note:

"In the addition of HX to vinyl halide, the halogen attached itself to the carbon atom, on which the halogen atom is already present."

2. Addition of halogens

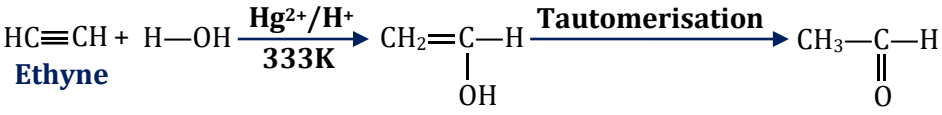


1,2-Dibromopropene **1,1,2,2-Tetrabromopropane**

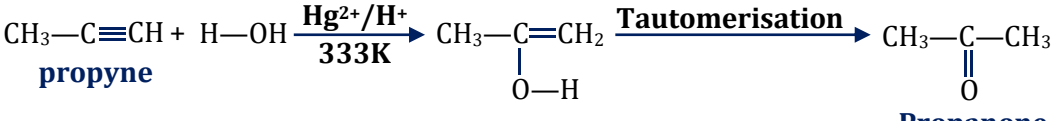
Reddish brown colour of the solution of bromine in carbon tetrachloride is decolourised so this reaction is used as a test for unsaturation.

3. Addition of water

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333K to form carbonyl compounds.



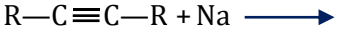
Ethyne **Ethanal**



propyne **Propanone**

Reaction of terminal alkynes R—C≡C—H

1. Reaction with sodium (Na)



TG: @Chalnaayaaar

Example :

$$CH_3—C\equiv C—H + Na \longrightarrow CH_3—C\equiv C^{\ominus}\,Na^{\oplus} + \frac{1}{2}H_2\uparrow$$

Sodium propynide

2. Reaction with Tollen's reagent (ammoniacal silver nitrate solution)

$AgNO_3 + NH_4OH$

$$R—C\equiv C—H \xrightarrow[NH_4OH]{AgNO_3 +} R—C\equiv C^{\ominus}\,Ag^{\oplus} + NH_4NO_3 + H_2O$$

(White ppt.)

$$R—C\equiv C—R \xrightarrow[NH_4OH]{AgNO_3 +} \text{No reaction}$$

$$\text{Alkene} \xrightarrow[NH_4OH]{AgNO_3 +} \text{No reaction}$$

3. Reaction with ammoniacal cuprous chloride solution.

($Cu_2Cl_2 + NH_4OH$)

$$R—C\equiv C—H \xrightarrow[NH_4OH]{Cu_2Cl_2 +} R—C\equiv C^{\ominus}\,Cu^{\oplus} + NH_4Cl + H_2O$$

(red ppt.)

$$R—C\equiv C—R \xrightarrow[NH_4OH]{Cu_2Cl_2 +} \text{No reaction}$$

$$\text{Alkene} \xrightarrow[NH_4OH]{Cu_2Cl_2 +} \text{No reaction}$$

1. Polymerisation

(a) Linear polymerisation :

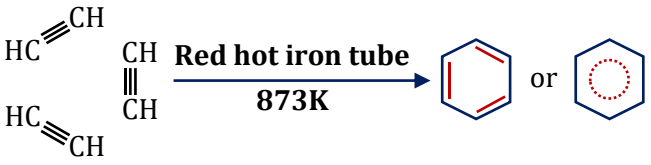
Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene.

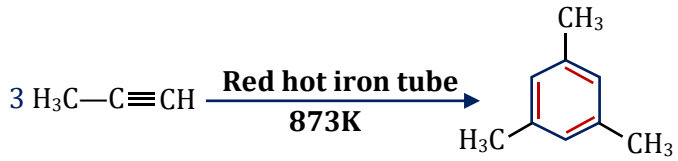
$$n(CH\equiv CH) \xrightarrow[\text{Catalyst}]{\text{High temp. / Pressure}} \text{-}(CH=CH—CH=CH)\text{-}_n$$

Polyethyne

(b) Cyclic polymerisation :

Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerisation.





Mesitylene

TG: @Chalnaayaaar

BEGINNER'S BOX-12

1. Propyne and HCl in presence of peroxide gives :

(1) 1,1–dichloro propane (2) 1,2–dichloro propane

(3) 1,3–dichloro propane (4) 2,2–dichloro propane

2. $CH_3—C\equiv CH \xrightarrow[(ii)H_2O_2/^-OH]{(I)BD_3} A$, A is

(1) $CH_3-\underset{\underset{D}{|}}{CH}-CH_2-OH$ (2) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-D$

(3) $CH_3-\underset{\underset{D}{|}}{CH}-CHO$ (4) $CH_3-\underset{\underset{D}{|}}{CH}-\underset{\underset{O}{\|}}{C}-D$

3. Which of the following decolourise 1% alkaline $KMnO_4$

(1) Propene (2) Propyne (3) 2-butyne (4) All of them

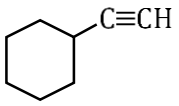
4. 1-Alkyne and 2 -Alkyne can not be distinguished by :

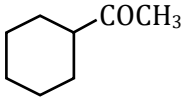
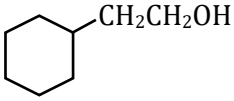
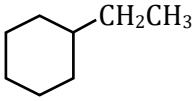
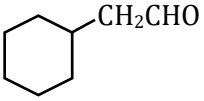
(1) Ammonical $AgNO_3$ (2) Baeyer's reagent (3) Br_2 in CCl_4 (4) 2 and 3 both

5. What is the main product of this reaction ?

$CH_3—CH\equiv CH \xrightarrow[\text{Excess}]{HCl\ (g)}$?

(1) $CH_3—\overset{\overset{Cl}{|}}{C}=CH_2$ (2) $CH_3—\underset{\underset{Cl}{|}}{CH}—\underset{\underset{Cl}{|}}{CH_2}$ (3) $CH_3—CH—CH\begin{matrix}Cl\\Cl\end{matrix}$ (4) $CH_3—\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}—CH_3$

6. Hydration of  in presence of H_2SO_4 / $HgSO_4$ gives

(1)  (2)  (3)  (4) 

7. Propyne and HCl in presence of peroxide gives :

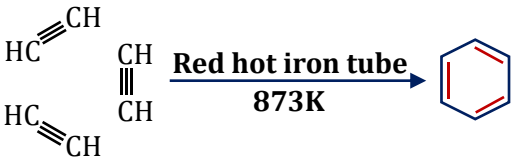
(1) 1,1–dichloro propane (2) 1,2–dichloro propane

(3) 1,3–dichloro propane (4) 2,2–dichloro propane

Aromatic Hydrocarbon

Preparation Methods of Benzene

1. Cyclic polymerisation of ethyne



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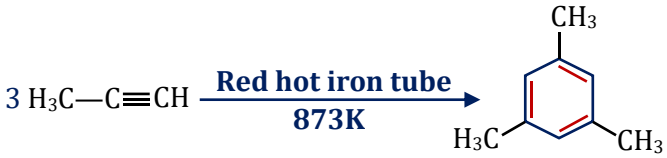
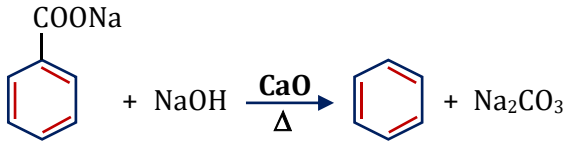


Mesitylene

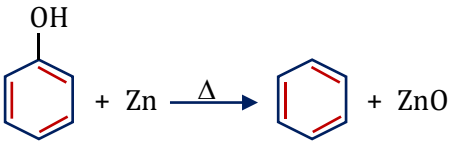
2. Decarboxylation of aromatic acids (Soda lime reaction)

Sodium salt of benzoic acid on heating with sodalime gives benzene.



3. Reduction of phenol

Phenol is reduced to benzene by passing its vapours over heated zinc dust.

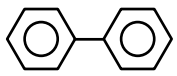
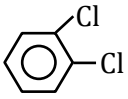
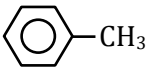


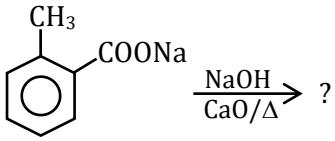
BEGINNER'S BOX-13

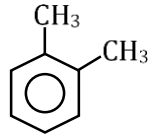
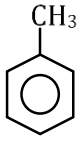
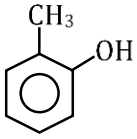
1. When n-heptane is reacted in the presence of Cr_2O_3 at high temprature & pressure then major product will be :-

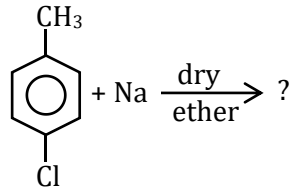
(1) Benzene (2) Toluene (3) Ethylbenzene (4) Phenol

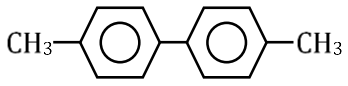
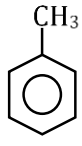
2. What will be major product if clorobenzene reacted with Na in the presence of dry ether :-

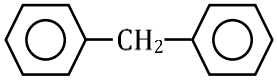
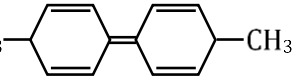
(1)  (2)  (3)  (4) None

3. 

(1)  (2)  (3)  (4)

4. 

(1)  (2) 

(3)  (4) 

TG: @Chalnaayaaar

Physical Properties of Benzene

(A) Aromatic hydrocarbons are non- polar molecules and are usually colourless liquids or solids with a characteristic aroma.

(B) Naphthalene balls are used in toilets and for preservation of clothes.

(C) Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents.

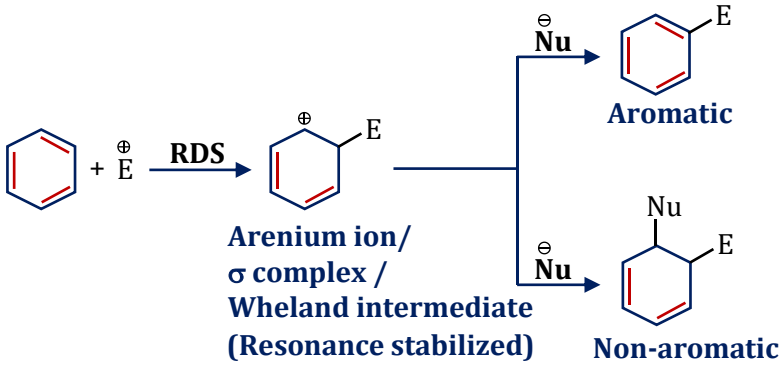
(D) They burn with sooty flame.

Chemical Properties of Benzene

Electrophilic Substitution Reaction (ESR)

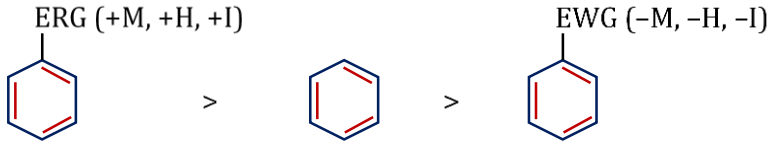
ESR is the characteristic reaction of benzene and its derivatives.

Mechanism



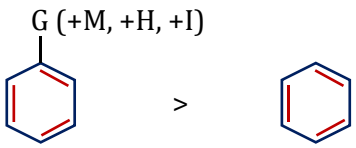
Note:

1. Rate towards ESR ∝ Nucleophilicity of benzene ring
   ∝ stability of σ complex

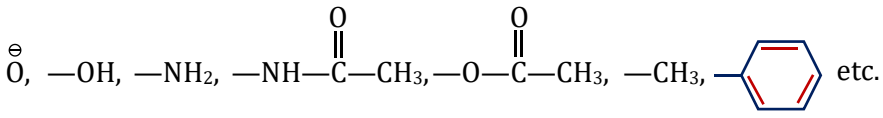


Activating Groups

Substituents which make ring more reactive than benzene are activating groups (rate towards ESR is more than benzene).



Example :



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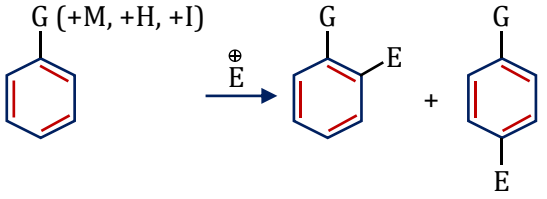
Note:

All activating groups are ortho-para directing.

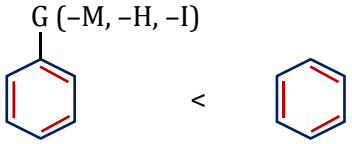
(Directs the incoming electrophile at ortho-para position)



Deactivating Groups

Substituents which make ring less reactive than benzene are deactivating groups

(rate towards ESR is less than benzene).



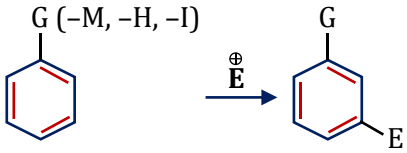
Example :

—NO_2, —COOH, —CHO, —CCl_3, —$\overset{\oplus}{N}H_3$ etc.

Note:

Generally, deactivating groups are meta directing.

(Directs the incoming electrophile at meta position)

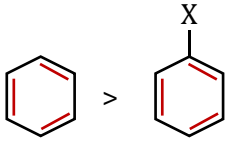


Exception

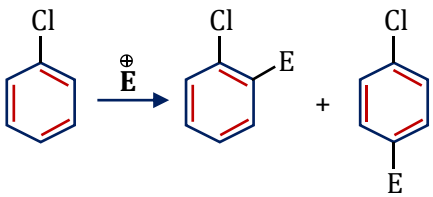
Halogens are weakly deactivating but ortho para directing.

Reactivity is controlled by inductive effect but orientation is controlled by mesomeric effect.

Rate towards ESR



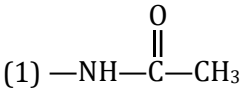
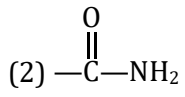
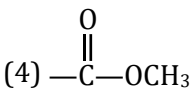
Attack of electrophile

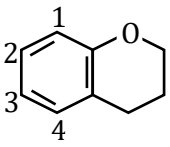


TG: @Chalnaayaaar

BEGINNER'S BOX-14

1. Which of the following group is ortho para director :-

(1)  (2)  (3) —C≡N (4) 

2.  Substitution takes place at the position.

(1) 1 (2) 2 (3) 3 (4) Both (1) and (3)

3. Correct order of reactivity of following compound with an electrophile :-

(I) p—CH_3—C_6H_4—CH_3 (II) C_6H_5—CH_3

(III) p—CH_3—C_6H_4—NO_2 (IV) p—O_2N—C_6H_4—NO_2

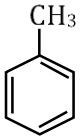
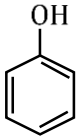
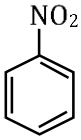
(1) I > II > III > IV (2) II > I > IV > III (3) III > II > I > IV (4) IV > III > II > I

4. Nitration of benzene is

(1) Nucleophilic substitution (2) Nucleophilic addition

(3) Electrophilic substitution (4) Electrophilic addition

5. Consider the following compounds :

(I) (II)  (III)  (IV) 

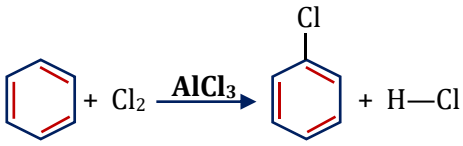
Correct order of their reactivity in electrophilic substitution reactions would be :-

(1) I > II > III > IV (2) IV > III > II > I (3) III > II > I > IV (4) III > IV > I > II

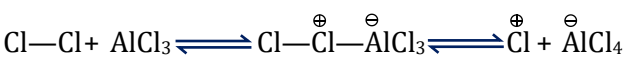
6. Which is meta directly group ?

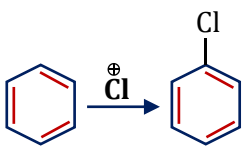
(1) $-O^{\ominus}$ (2) $-\overset{\oplus}{N}H_3$ (3) –NH–CH_3 (4) –O–$COCH_3$

1. Halogenation reaction



Mechanism





Electrophile:– Chloronium ion (Halonium ion)

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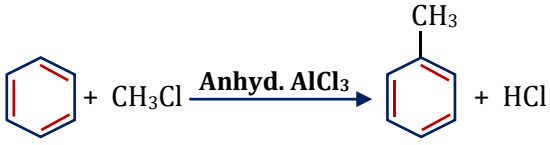
2. Friedel crafts alkylation

When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed.

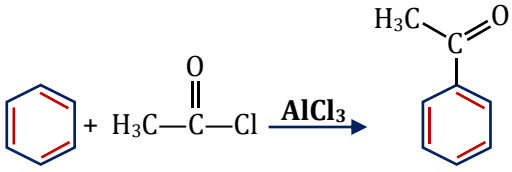


Toluene

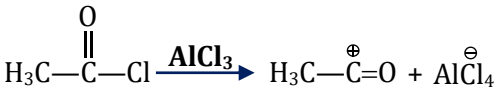
Carbocation forms, So rearrangement occurs (if possible) before attack on benzene or derivatives.

3. Friedel crafts acylation

The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ($AlCl_3$) yields acyl benzene.

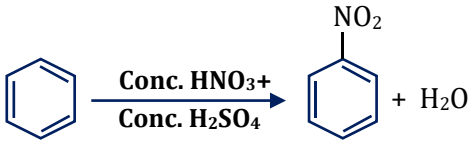


(Acetophenone)

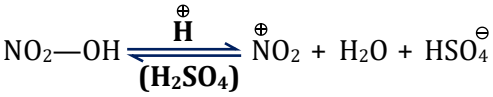


4. Nitration reaction

In nitration reaction, -NO_2 group is introduced in an aromatic ring.



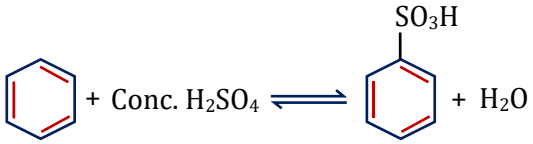
Mechanism



Electrophile :- Nitronium ion ($\overset{\oplus}{NO_2}$)

Note: If $KHSO_4$ is added to the reaction mixture rate of reaction decreases, due to common ion effect.

5. Sulphonation reaction (By conc. H_2SO_4 or oleum)



Benzene sulphonic acid

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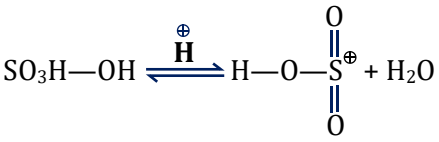
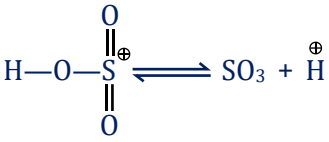
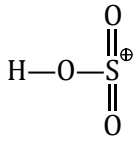
Mechanism

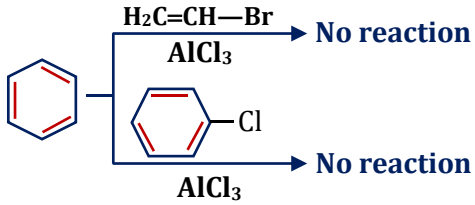




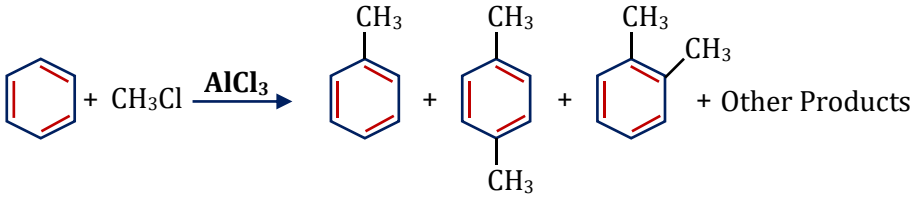
Electrophile:  or SO_3

Important Points

1. Vinyl halide and aryl halide cannot be used as halide component in Friedel Crafts alkylation.

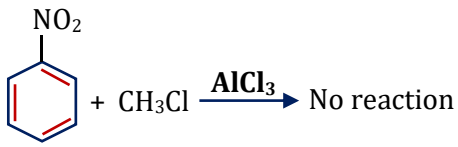


2. Polyalkylation is a major problem in Friedel Crafts Alkylation as the formed product is more reactive compared to reactant.

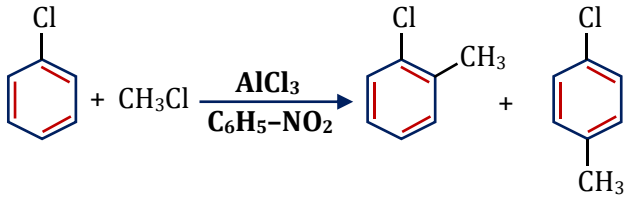


3. In presence of strongly deactivating groups (meta directing groups $-NO_2$, $-COOH$, $-CHO$, $-\overset{\oplus}{N}H_3$ etc.) Friedel Crafts reaction (alkylation and acylation) does not take place.

Example :



Nitrobenzene can be used as solvent in Friedel Crafts reaction.



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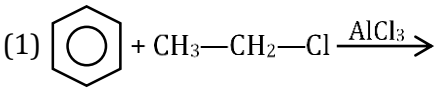
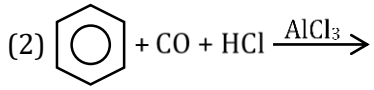
BEGINNER'S BOX-15

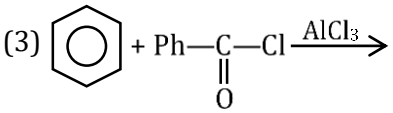
1. The active species in the nitration of benzene is

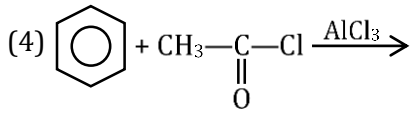
(1) NO_2^+ (2) HNO_3 (3) NO_3^- (4) NO_2^-

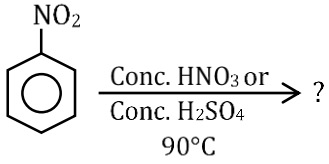
2. Which is Friedel craft acetylation ?

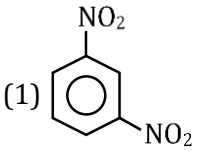
(1) 

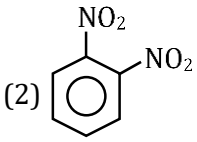
(2) 

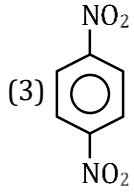
(3) 

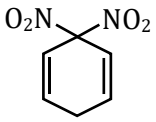
(4) 

3. 

(1) 

(2) 

(3) 

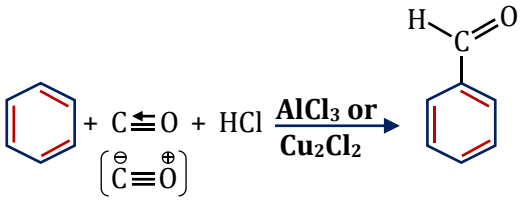
(4) 

4. In Halogenation of benzene, $AlCl_3$ act as –

(1) Halogen carier (2) Lewis acid

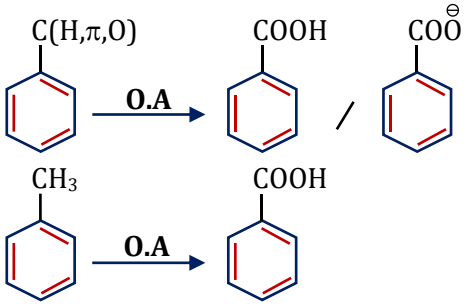
(3) Electrophile initiator (4) All

6. Gattermann Koch Reaction



7. Oxidation using

1. $KMnO_4/\overset{\oplus}{H}$
2. $KMnO_4/\overset{\ominus}{O}H/\Delta$
3. $K_2Cr_2O_7/\overset{\oplus}{H}$



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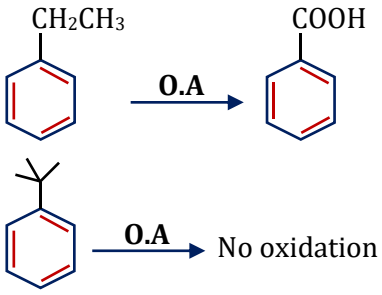
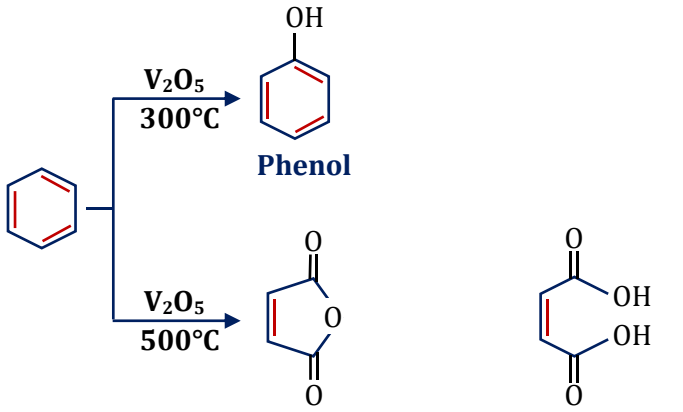
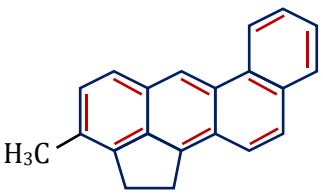


8. Oxidation using V_2O_5

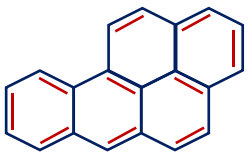


Carcinogenicity and toxicity

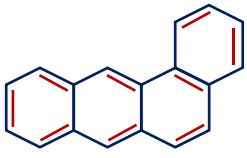
- Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property.
- Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum.
- They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer.



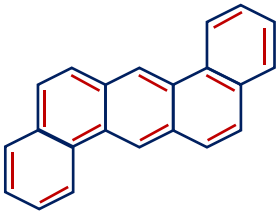
3-Methylcholanthrene



1, 2-Benzpyrene



1, 2-Benzanthracene



1, 2, 5, 6-Dibenzanthracene

TG: @Chalnaayaaar

BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3
	Ans.	2	3	2

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7
	Ans.	2	4	3	2	1	2	4

BEGINNER'S BOX-3	Que.	1	2	3	4
	Ans.	3	3	2	4

BEGINNER'S BOX-4	Que.	1	2	3	4	5
	Ans.	1	3	1	3	2

BEGINNER'S BOX-5	Que.	1	2	3
	Ans.	3	2	2

BEGINNER'S BOX-6	Que.	1	2	3	4	5	6	7	8	9
	Ans.	3	3	1	2	1	2	3	4	1

BEGINNER'S BOX-7	Que.	1	2	3	4	5
	Ans.	2	1	1	3	4

BEGINNER'S BOX-8	Que.	1	2	3
	Ans.	3	1	1

BEGINNER'S BOX-9	Que.	1	2	3
	Ans.	1	3	1

BEGINNER'S BOX-10	Que.	1	2
	Ans.	3	1

BEGINNER'S BOX-11	Que.	1	2
	Ans.	3	1

BEGINNER'S BOX-12	Que.	1	2	3	4	5	6	7
	Ans.	4	3	4	4	4	1	4

BEGINNER'S BOX-13	Que.	1	2	3	4
	Ans.	2	1	2	1

BEGINNER'S BOX-14	Que.	1	2	3	4	5	6
	Ans.	1	4	1	3	3	2

BEGINNER'S BOX-15	Que.	1	2	3	4
	Ans.	1	4	1	4

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